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Recent Developments in Aqueous Soluble Organic Flow Battery Systems

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Pacific Northwest National Laboratory

Support from DOE Office of Electricity Delivery & Energy Reliability Energy Storage Program

Energy Storage Systems Program Review
Washington DC
September 26, 2016

Redox Flow Batteries

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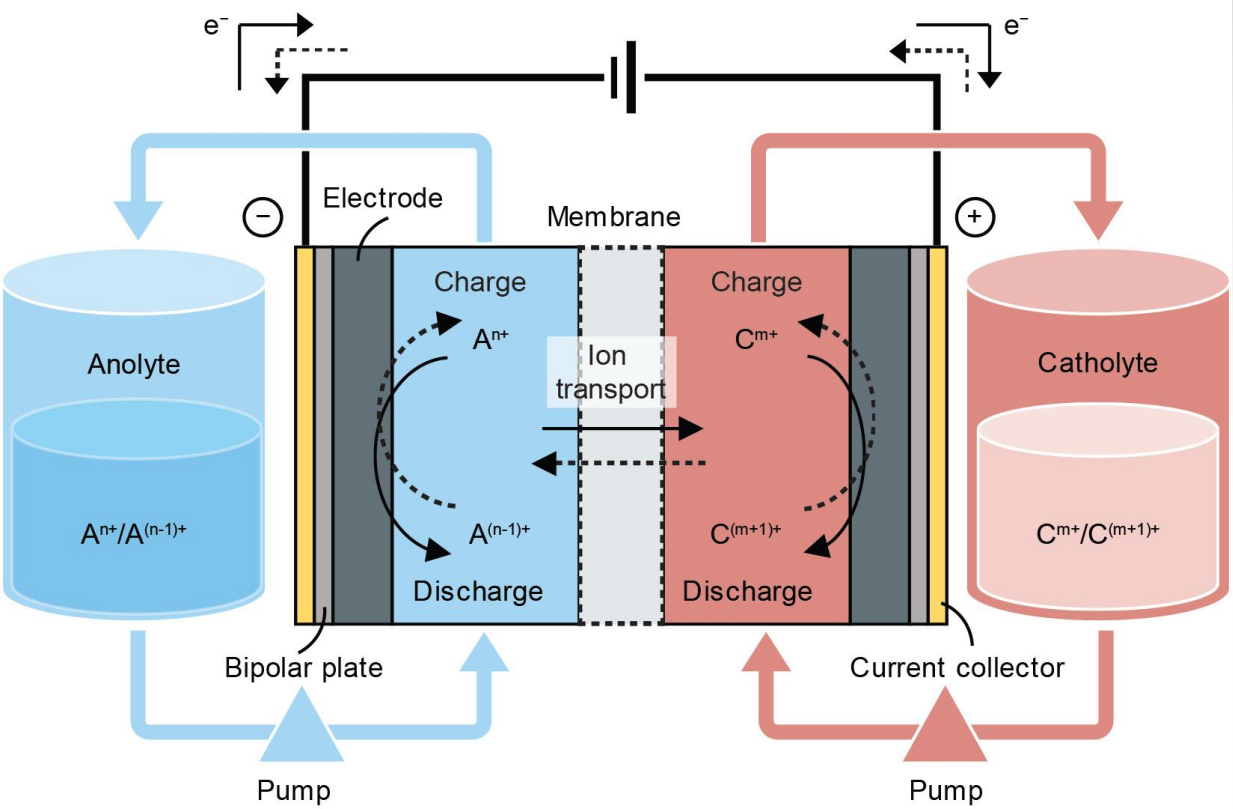

Key Aspects

- ***Power and Energy are separate enabling greater flexibility and safety.***
- ***High safety***
- Suitable for wide range of applications 10's MW to ~ 5 kw
- Wide range of chemistries available.
- Low energy density ~ 30 Whr/kg

Project Overview

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- **Energy Storage Challenge**
  - Development of cost and performance competitive RFBs for stationary energy storage application.
- **Project Objective**
  - Identify and develop future RFB systems with potential to reach cost target.
- **Accomplishments**
  - Identify and synthesis of new organic redox couples.
  - Development of cost competitive new redox flow chemistries.
  - >10 publications, 1 patent applications, 2 patents granted in 2016

Mixed-acid VRB Development

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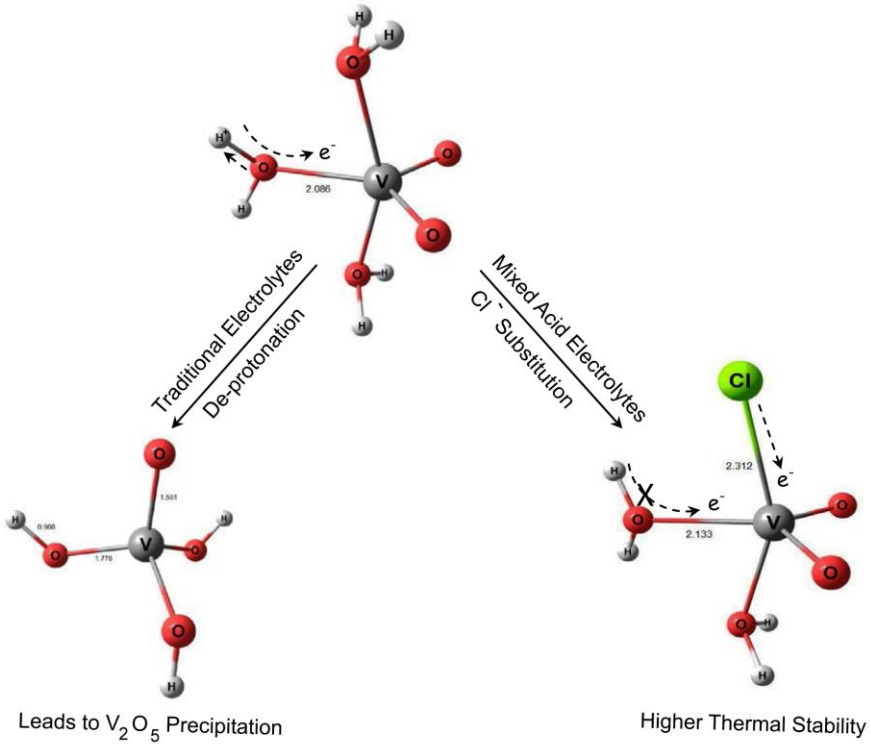
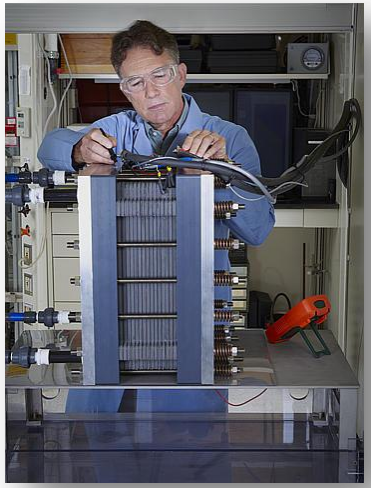
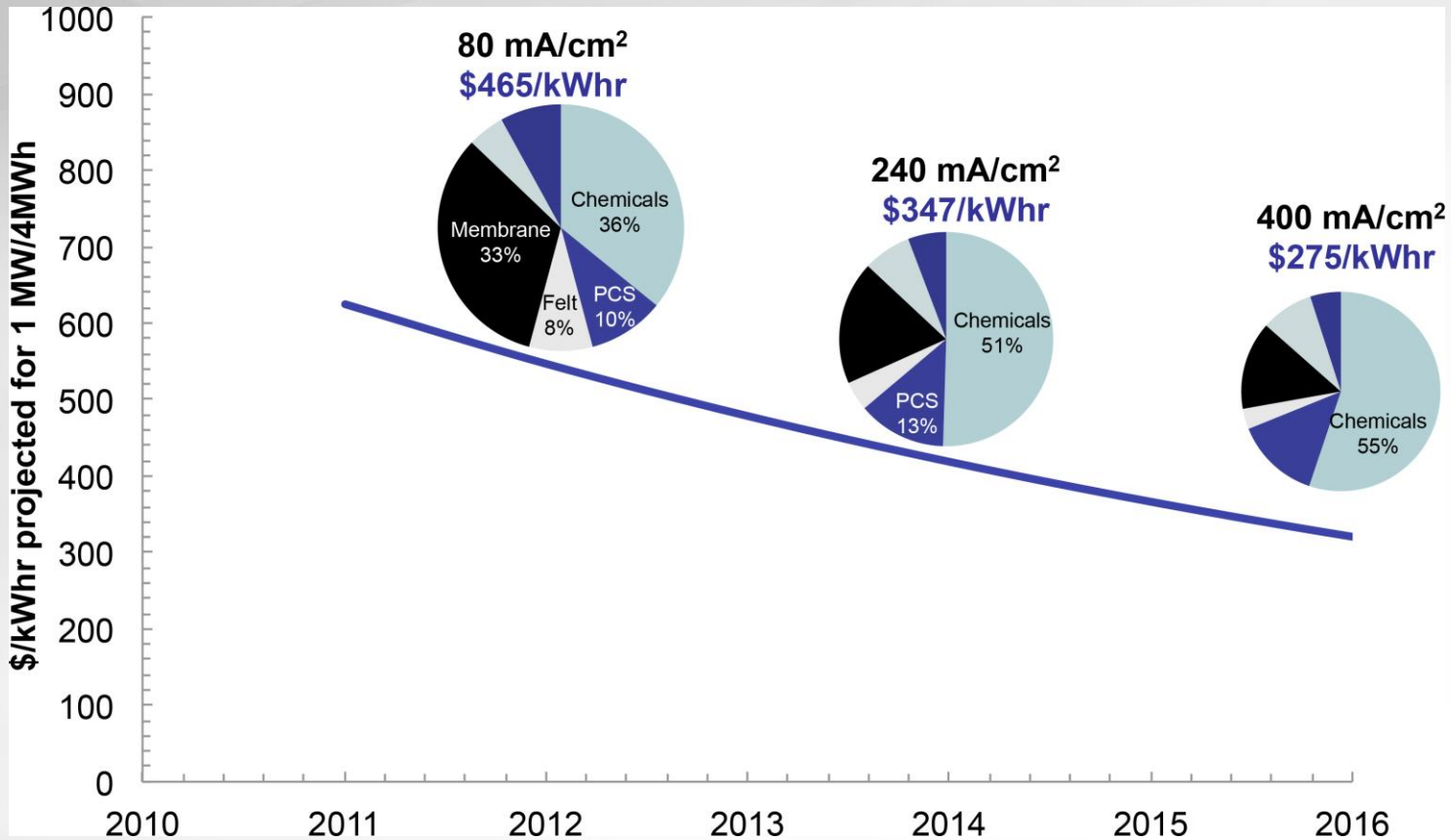


Leads to V_2O_5 Precipitation

Higher Thermal Stability



Shifting Cost Paradigm



Existing redox systems, advantages/issues

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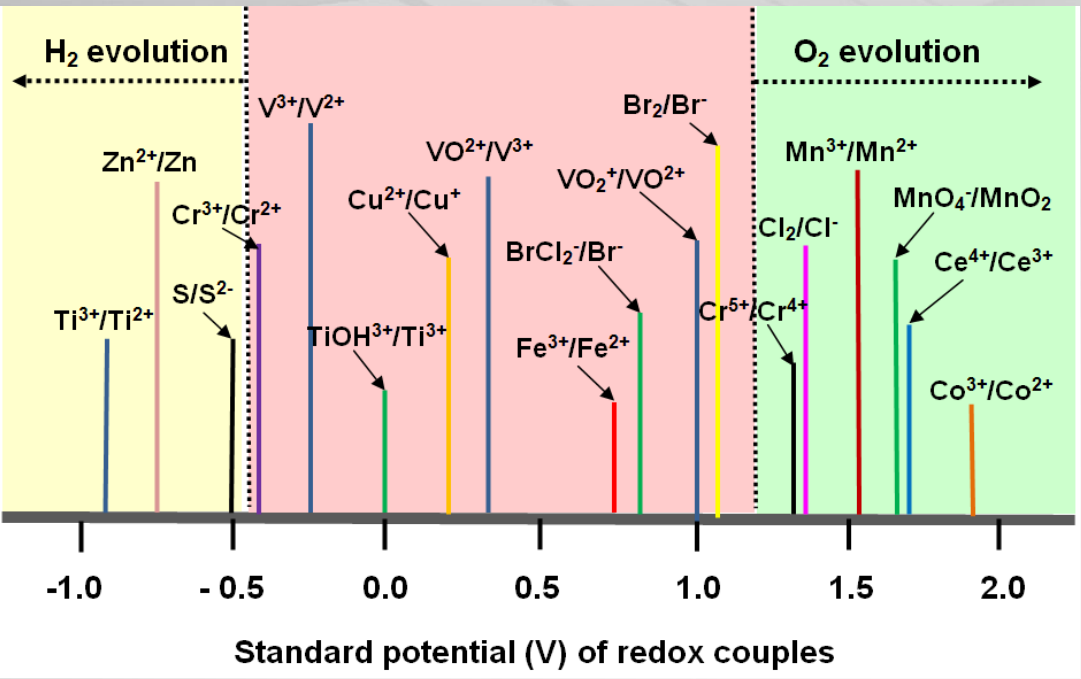
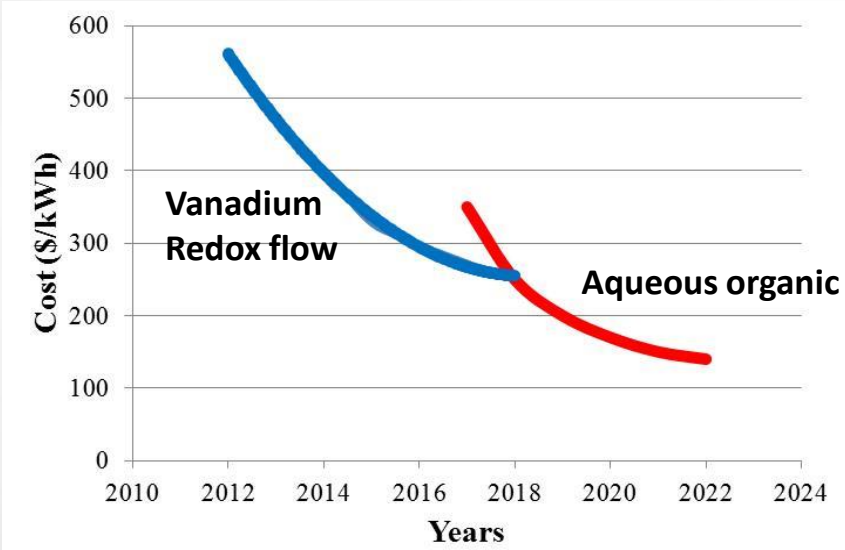


V: 120 ppm, $27/kg, high oxidation states toxic
Fe: 5.6 wt. %, $2/kg, nontoxic
Cr: 102 ppm, $2.8/kg, Cr^{5+} toxic
Ce: 60 ppm, $12/kg, moderately toxic
Mn: 0.1 wt.%, $2.8/kg, powders toxic
Ti: 4 ppm, $6.5/kg, nontoxic
S: 350 ppm, $1-30/kg, oxide and hydride toxic
Cl: 150 ppm, $1.5-3.0/kg, toxic
Br:2.4 ppm, $1.5/kg, toxic
Zn: 70 ppm, $1.8/kg, nontoxic
Cu: 60 ppm, $6.6/kg, nontoxic
Co: 25 ppm, $44/kg, nontoxic



Redox Flow Battery Based on Low-cost Redox Couples

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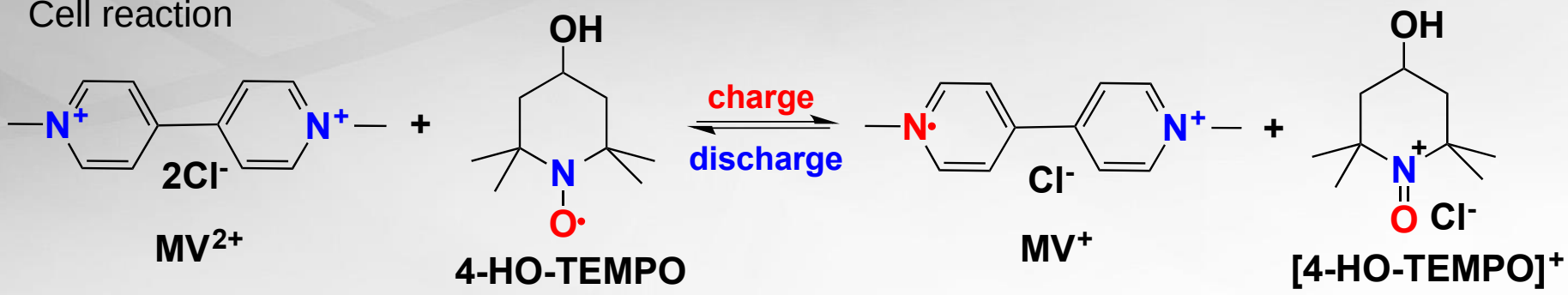
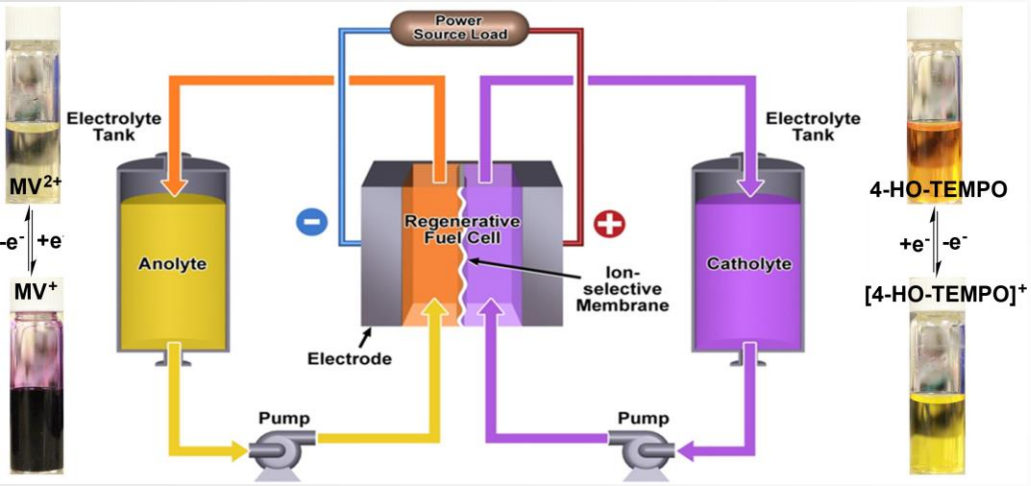
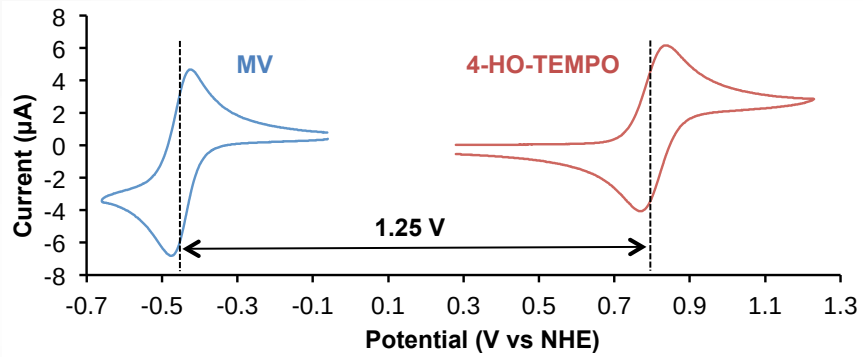
Cell reaction







Flow Cell Performance – High Concentration

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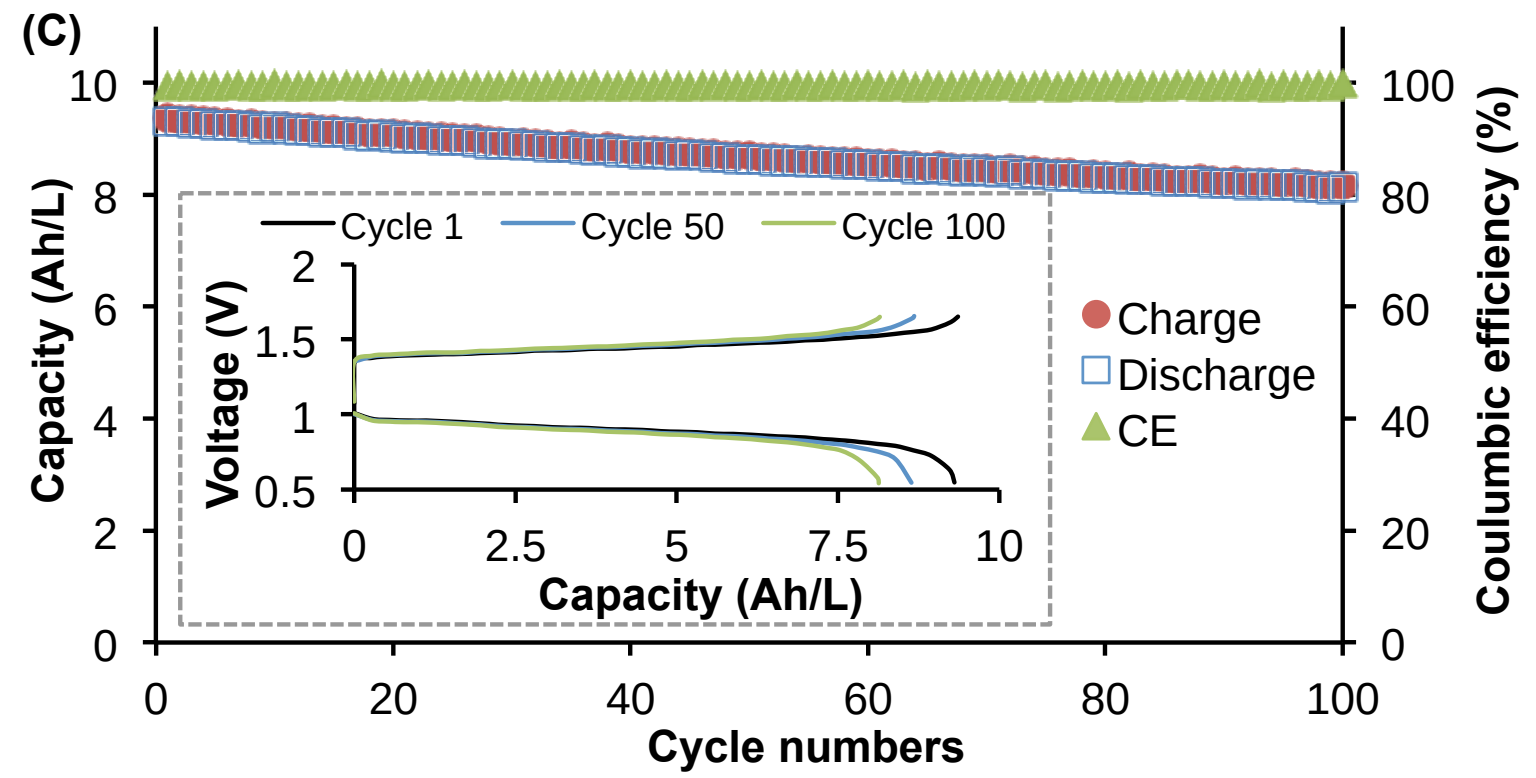

Capacity and coulombic efficiency vs cycling numbers of the cell at 40 mA/cm^2. Conditions: anolyte, 0.5 M **MV** in 1.5 M NaCl aqueous solution; catholyte, 0.5 M **4-HO-TEMPO** in 1.5 M NaCl aqueous solution; flow rate, 20 mL/min; AMV anion membrane. No remixing.

Chemical Stability of HO-TEMPO+

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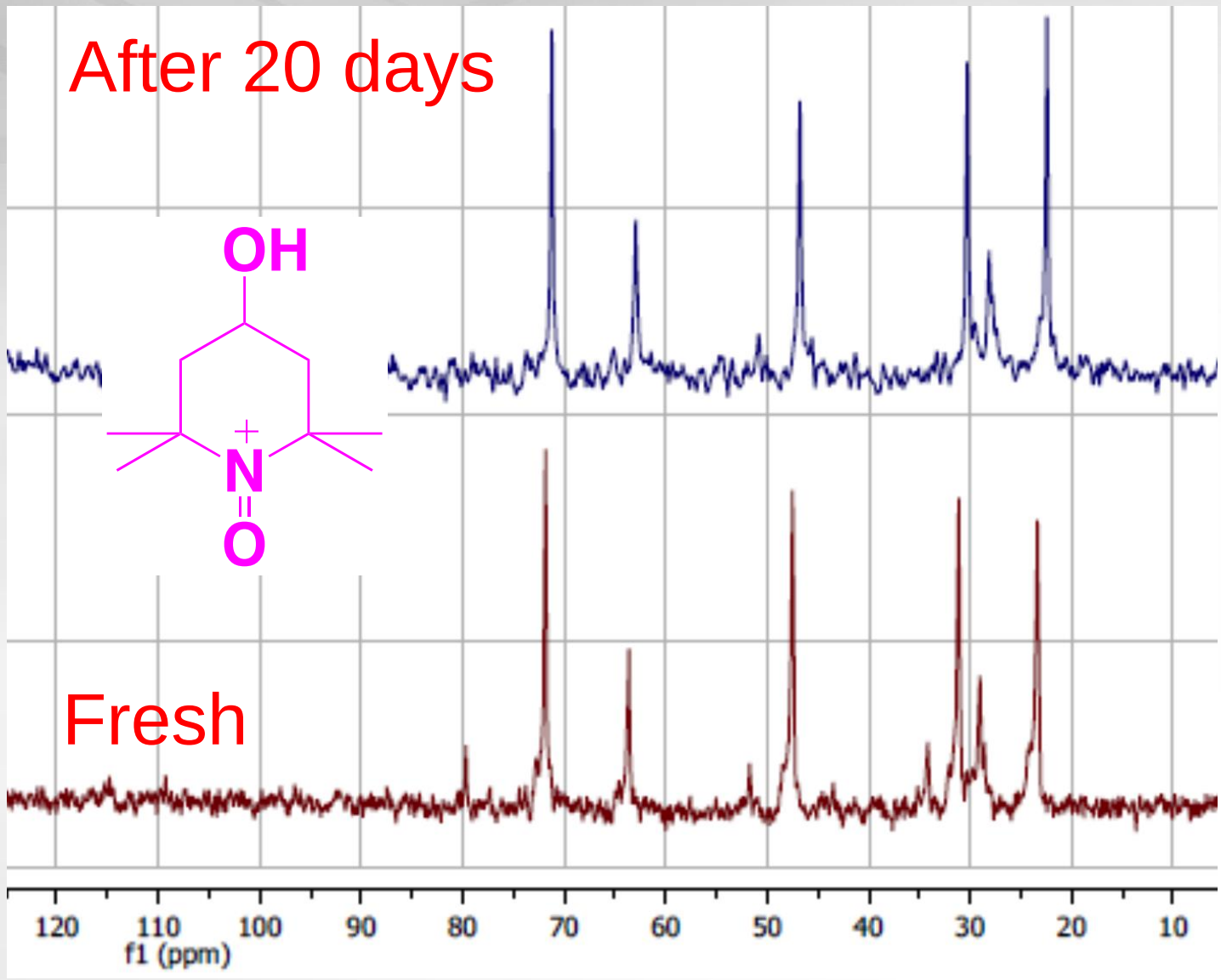

Chemical Stability of MV•—

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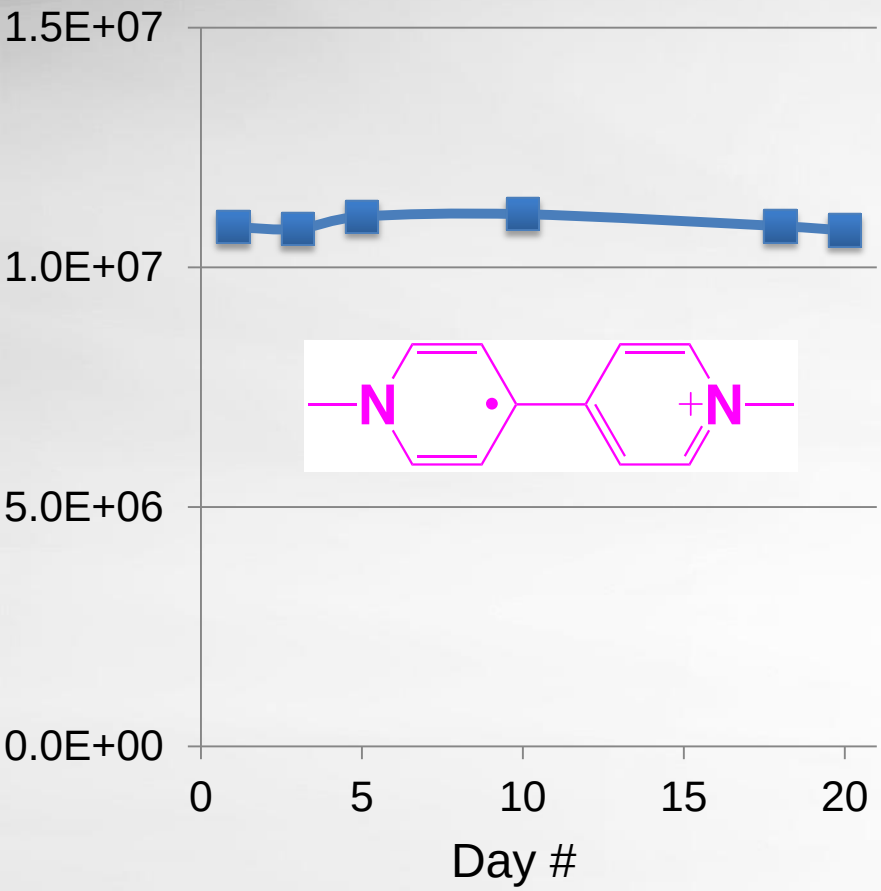
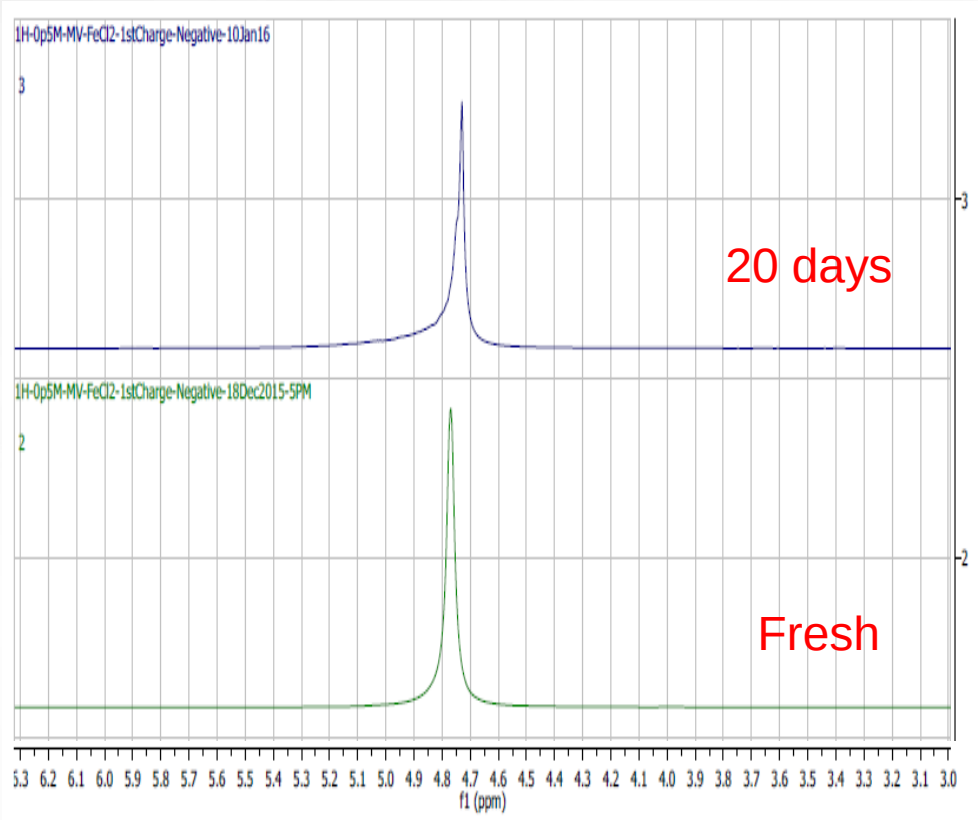
ESR Integral



No NMR signal



NMR Diagnostics on Cross Over (Catholyte)

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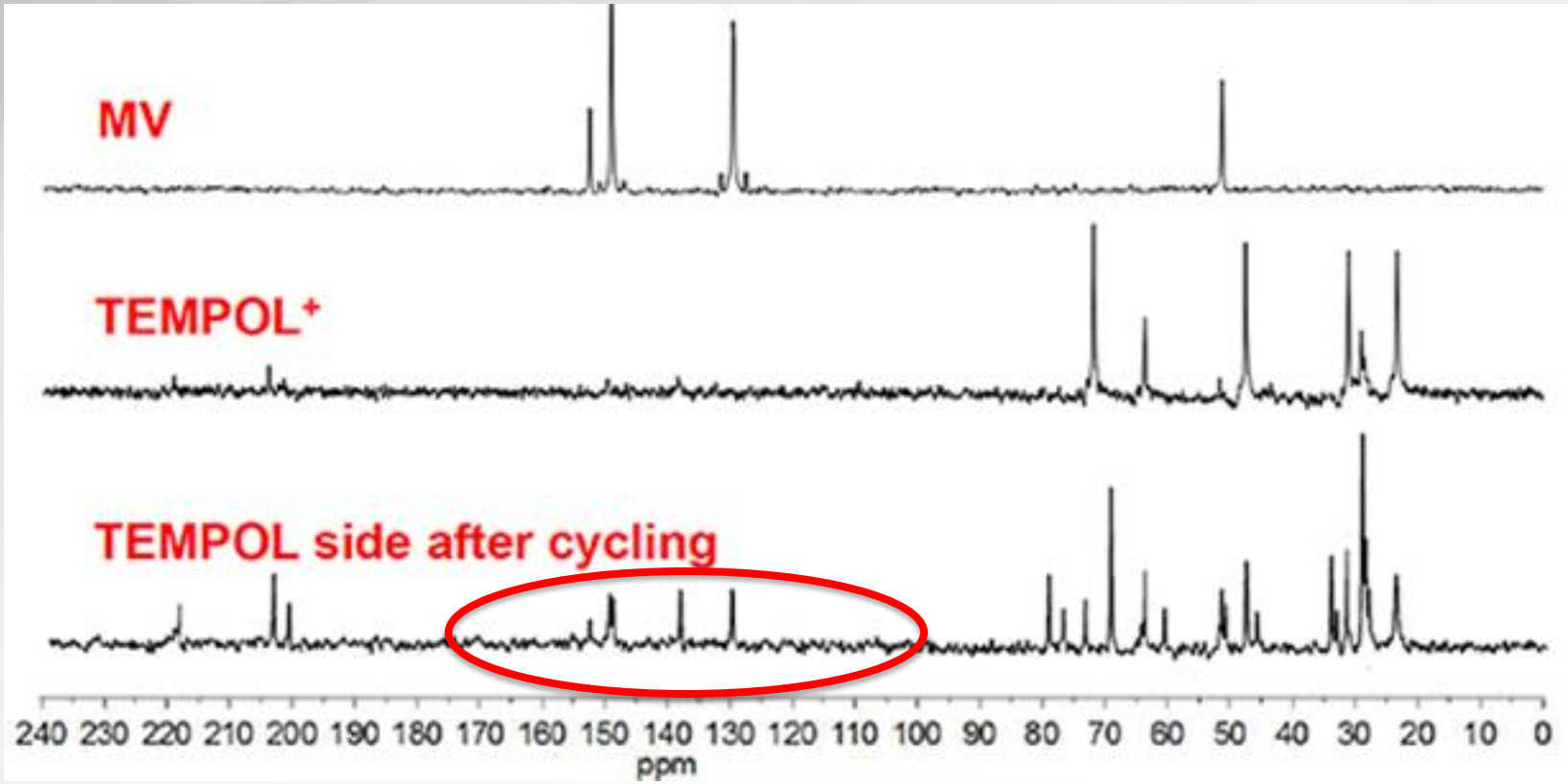

NMR Diagnostics on Cross Over (Anolyte)

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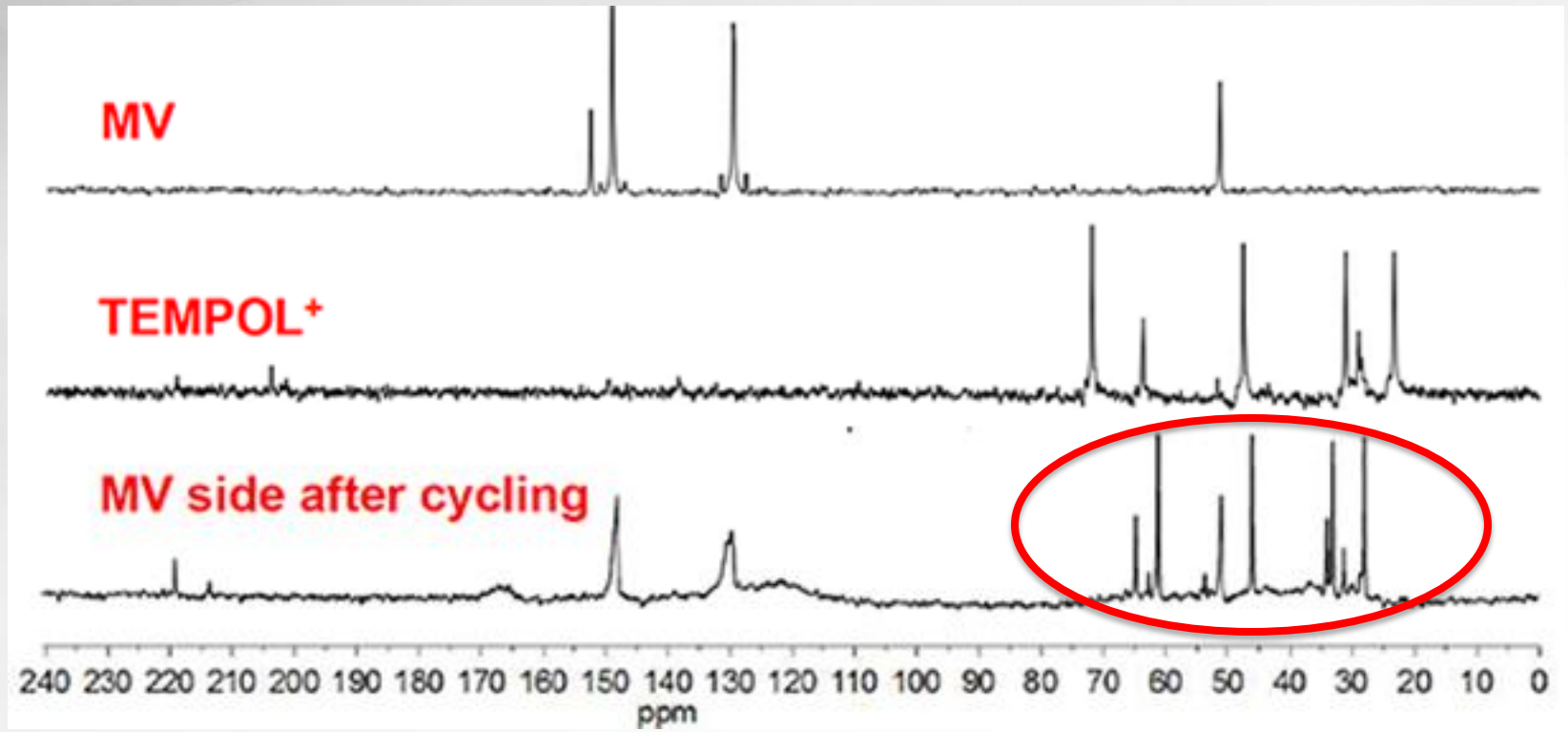

New Organic-Inorganic RFB Chemistry

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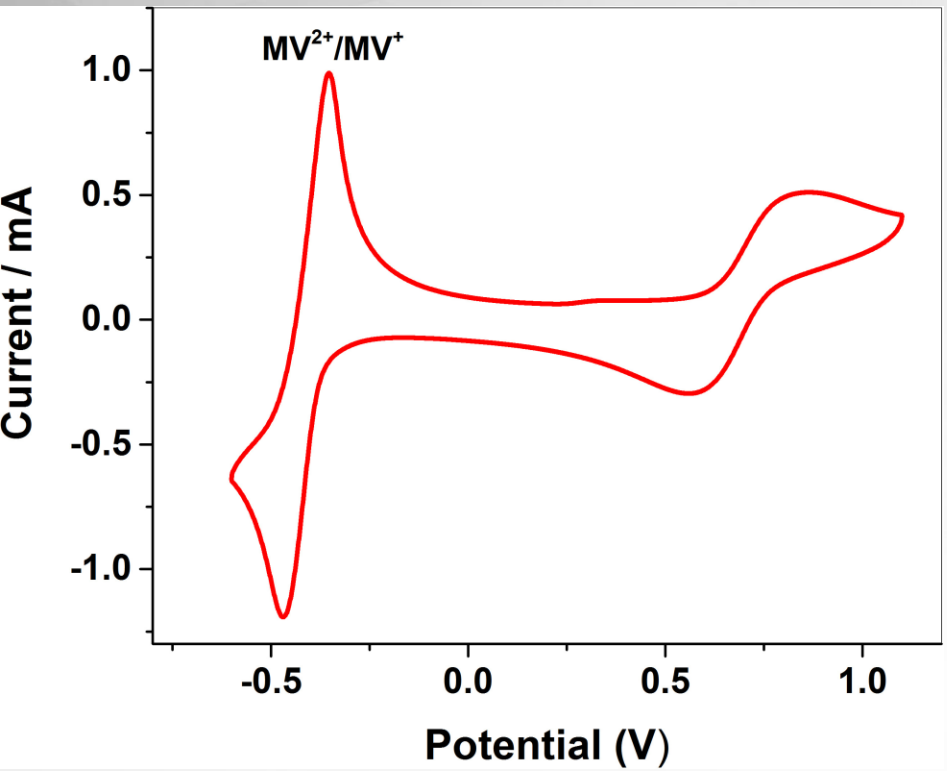

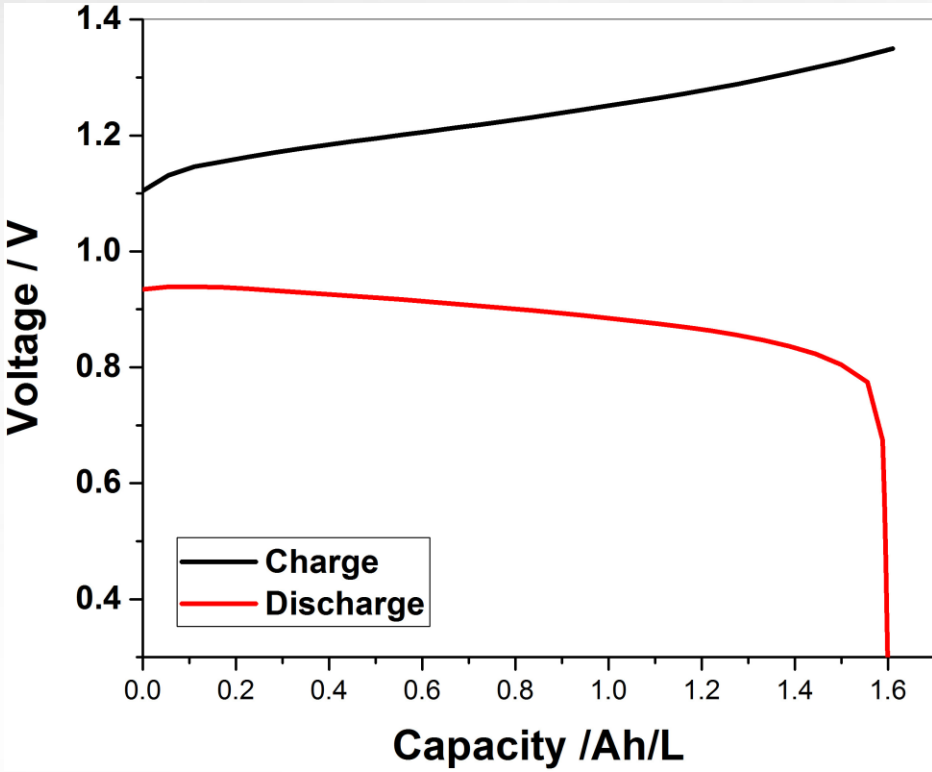

CV and voltage profile of the MV-Cation redox chemistry .

New Organic-Inorganic RFB Chemistry

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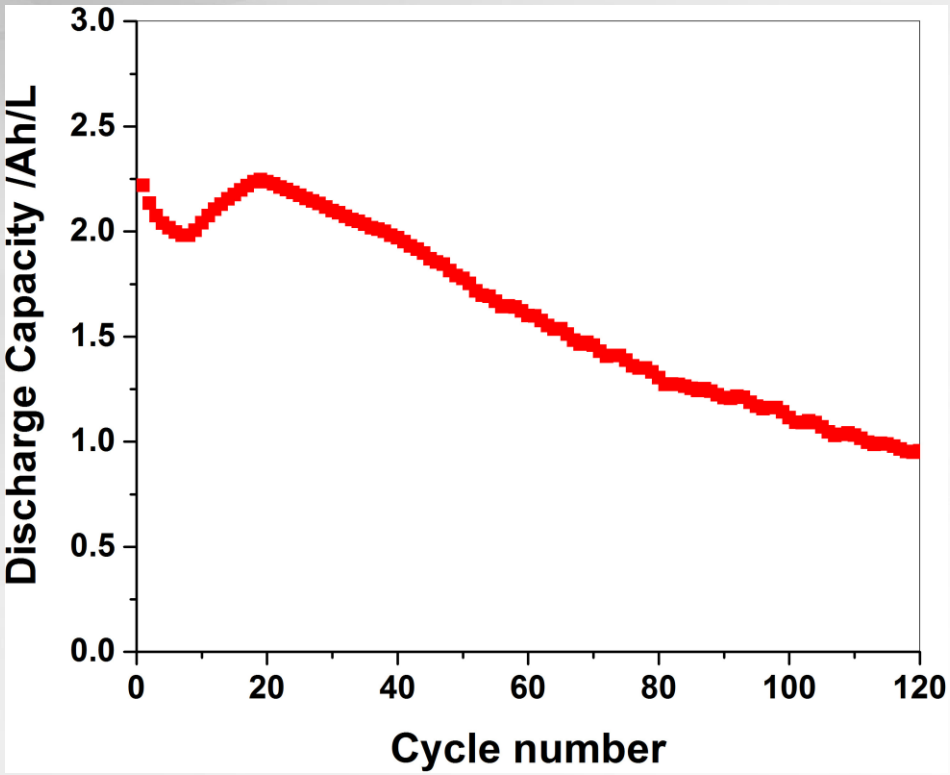

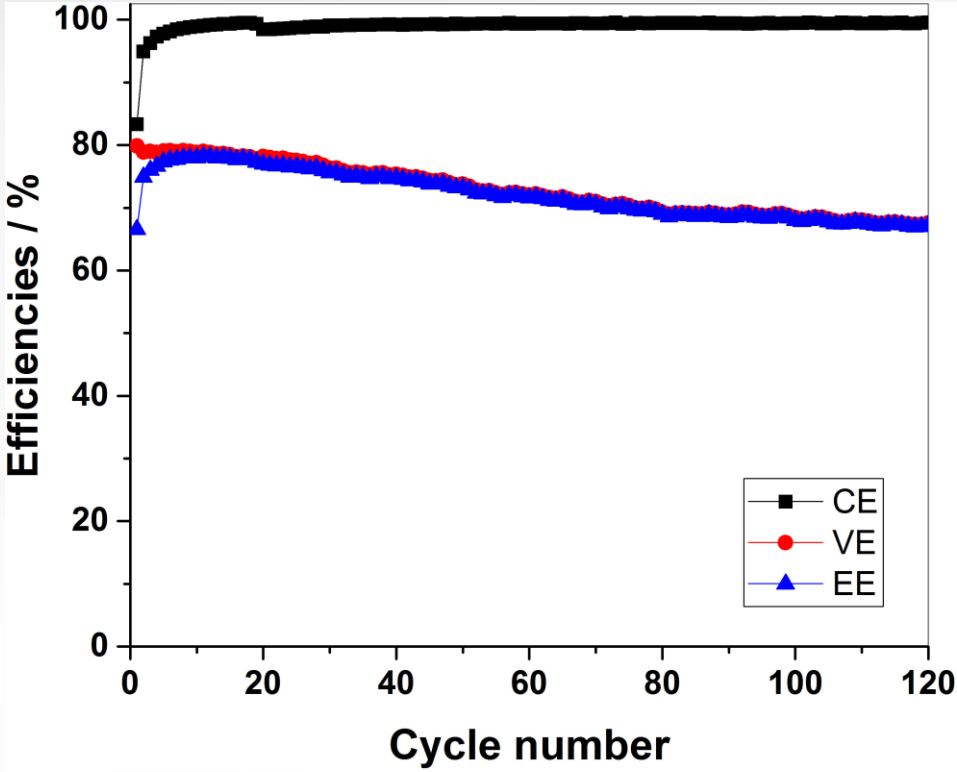

Cycling capacity and efficacies of the MV-Cation redox chemistry .

Cycling Performance and Improvement

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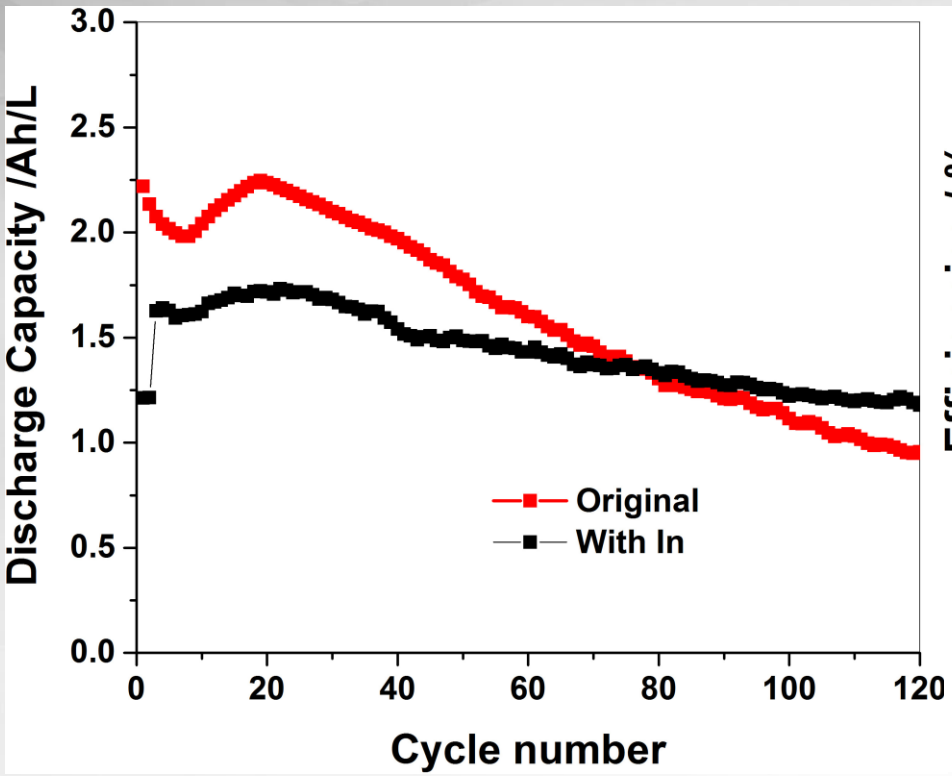

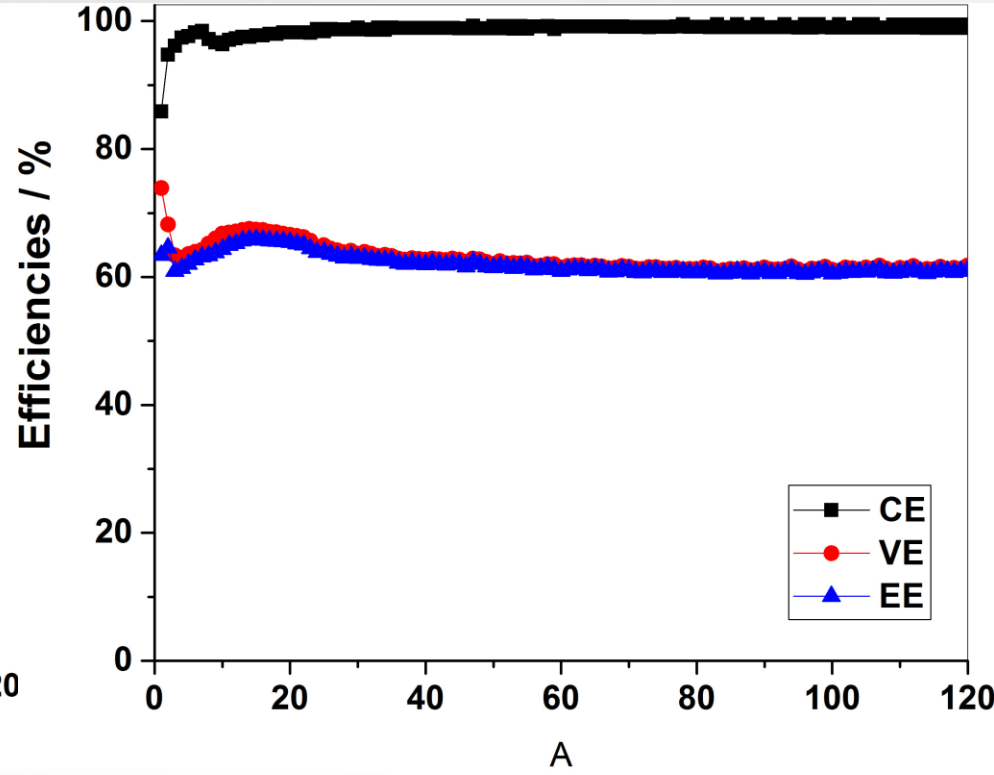

Cycling capacity and efficacies of the MV-Cation redox chemistry with hydrogen mitigation agent.

New Redox Chemistry

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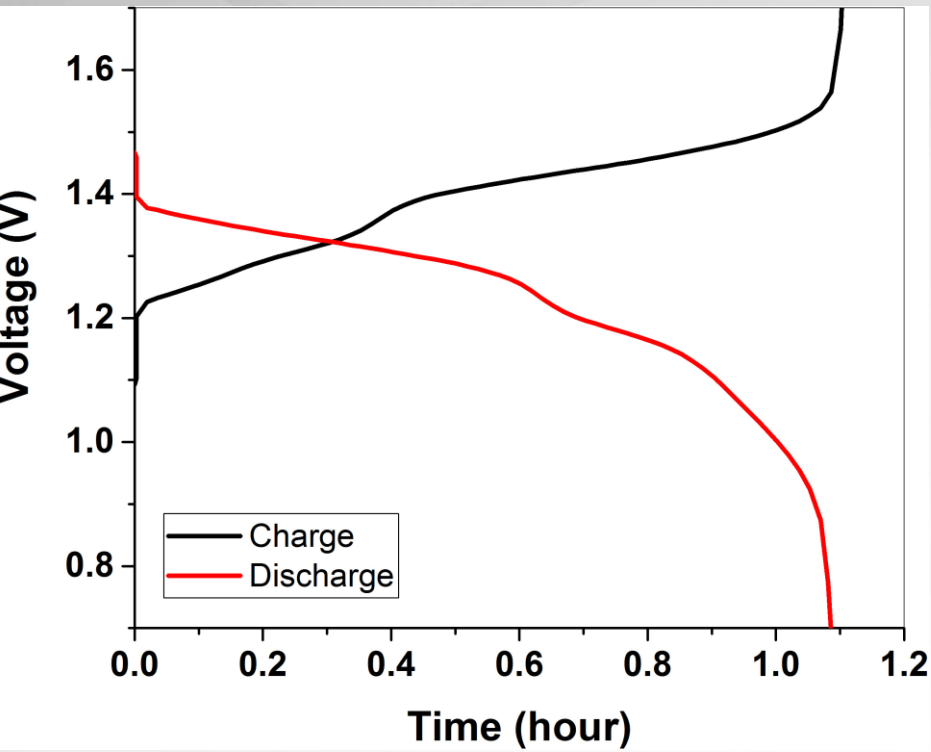

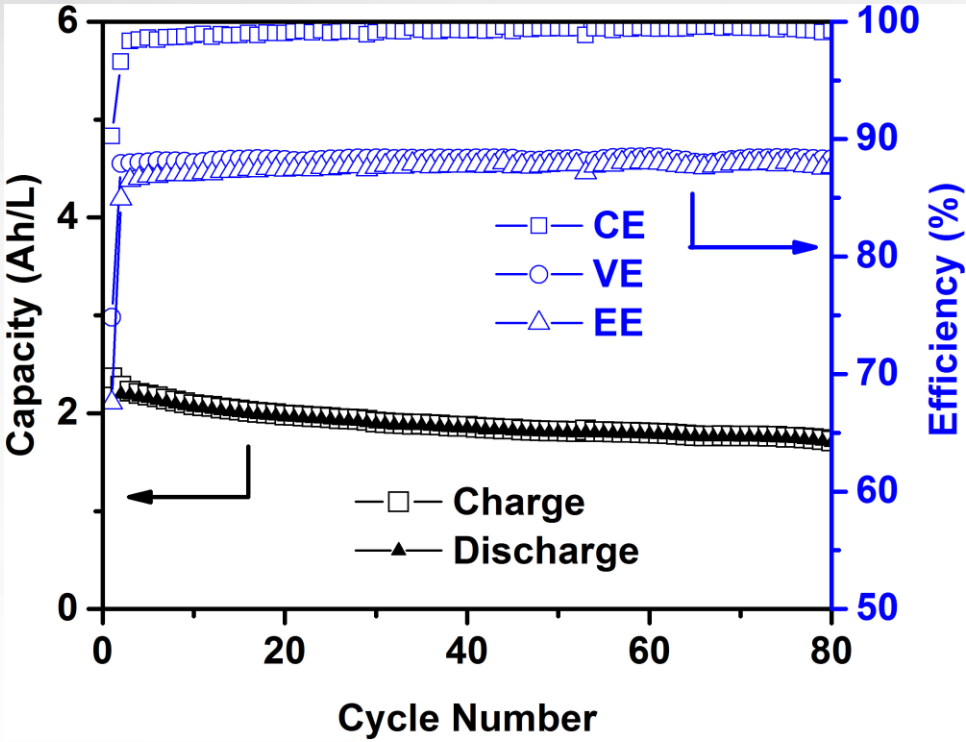

Conclusions

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- The capacity decay mechanism of the MV-HO-TEMPO redox flow system is identified.
- Two new low-cost organic redox chemistries have been developed with initial successful performance.

Future work

- Continuous optimization of the current system.
  - Improving the current density through electrolyte optimization;
  - Identify and develop low resistance membrane;
- Discover and identify new redox flow chemistry with potentials to reach cost and performance target.

Acknowledgements

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- External collaborators
  - Sandia National Laboratory